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Optoelectronic properties of methyl-terminated germanane

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Abstract
Germanane is a two-dimensional, strongly confined form of germanium. It presents an interesting combination of (i) ease of integration with CMOS technology, (ii) low toxicity, and (iii) electronic confinement which transforms the indirect bandgap of the bulk material into a direct bandgap featuring photoluminescence. However, the optoelectronic properties of this material remain far less investigated than its structural properties. Here, we investigate the photoluminescence and transport properties of arrays of methyl-terminated germanane flakes. The photoluminescence appears to have two contributions, one from the band edge and the other from trap states. The dynamics of the exciton appear to be in the range of 1–100 ns. Conduction in this material appears to be p-type, while the photoconduction time response can be made as short as 100 μs.

Disciplines
Atomic, Molecular and Optical Physics | Chemical Engineering | Engineering Physics

Comments
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ABSTRACT

Germanane is a two-dimensional, strongly confined form of germanium. It presents an interesting combination of (i) ease of integration with CMOS technology, (ii) low toxicity, and (iii) electronic confinement which transforms the indirect bandgap of the bulk material into a direct bandgap featuring photoluminescence. However, the optoelectronic properties of this material remain far less investigated than its structural properties. Here, we investigate the photoluminescence and transport properties of arrays of methyl-terminated germanane flakes. The photoluminescence appears to have two contributions, one from the band edge and the other from trap states. The dynamics of the exciton appear to be in the range of 1–100 ns. Conduction in this material appears to be p-type, while the photoconduction time response can be made as short as 100 μs.

Nanocrystals have raised substantial interest over the past few years owing to their broadly tunable band edge energy, ranging from the ultraviolet to terahertz spectral regions.[1,2] Nanocrystals are now commonly used as green light-emitters for display technologies[3] or as chlorophyll-optimized down-converters for agricultural lighting. In all these applications, nanocrystals are optically pumped. More advanced applications such as light-emitting diodes (LEDs) or photodetectors[4] will require films of nanocrystals with suitable transport properties.

Currently, most nanocrystals are based on II–VI and III–V compound semiconductors that possess optical properties in the visible range but contain toxic elements and are difficult to integrate with CMOS technology.[5] In this sense, nanocrystals made from Group IV compounds are of utmost interest. However, Si[6,7] and Ge[8,9] nanocrystals have been far less investigated than other materials such as CdSe and PbS, in particular, due to their sensibility to oxidation.

Beyond these 0D quantum dots, 2D forms of Ge and Si, analogous to graphene, have also generated strong interest in recent years. Atomically thin sheets of Si and Ge (known as silicene[10] and germanene,[11] respectively) have been proposed as alternatives to graphene; however, their feasibility and stability remain controversial.[12] In addition, the bandgap of silicene and germanene is expected to be very narrow,[13] which make them poor candidates for optoelectronic applications in spite of their low effective masses induced by Dirac cones. In addition and in contrast to graphene, silicene and germanium cannot be separated from their substrate, which makes their device integration even more challenging. It is nevertheless possible to grow 2D sheets of Si and Ge terminated by either hydrogen or methyl groups.[14–18] These forms of weakly coupled Si and Ge 2D-flakes are called silicane and germanane,[19–21] and they present a strong confinement leading to a bandgap (1.8 eV for germanane) compatible with electronic and optical applications in the visible region. In addition, their effective masses are expected to be small, which could lead to high carrier mobilities.[22] While the electronic structure[23] and structural properties[22,24] of these materials have been widely investigated,

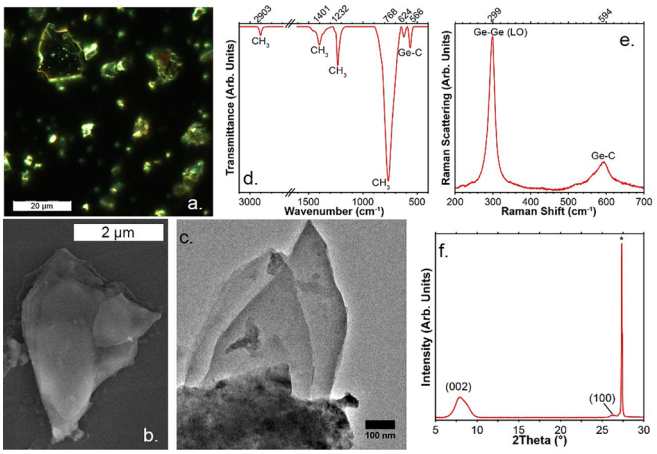

FIG. 1. Dark-field optical (a), scanning electron (b), and transmission electron (c) microscopy images of the methyl-terminated germanane flakes. FTIR (d) and Raman (e) spectra of methyl-terminated germanane powder. (d) Powder X-ray diffraction pattern of methyl-terminated germanane; the narrow peak highlighted with an "asterisk" corresponds to bulk Ge.

especially by the Goldberger group,[14] device integration remains limited.[25–27] Here, we investigate the optoelectronic properties of methyl-terminated germanane. We unveil their transport and spectroscopic properties which will be of utmost interest for future design of devices based on germanane.

We synthesized methyl-terminated germanane flakes by modifying a procedure reported by Jiang *et al.*,[14] see the supplementary material for details. The obtained flakes have large lateral dimensions reaching several microns, as revealed by microscopy images in Figs. 1(a)–1(c). These germanane flakes are composed of stacks of individual layers (20–50 nm in thickness typically) of methyl-terminated germanane, as revealed by the TEM image, see Fig. 1(c). Fourier-transform infrared (FTIR) spectroscopy confirms the presence of methyl termination, with vibrational modes arising from C-H and Ge-C bonds, see Fig. 1(d). The Raman spectrum [see Fig. 1(e)] reveals a main contribution appearing at 299 cm^{-1} which is associated with the E_{2g} mode.[21,28] A second contribution arising from the methyl functionalization appears at 594 cm^{-1}. The X-ray diffraction[15,18,29] [Fig. 1(f)], in particular, reveals a peak around $2\theta \approx 7.9°$, which, along with Raman and Fourier transform infrared spectroscopy, confirms that the sample contains Ge sheets that are terminated with $-CH_3$ groups.[15] From Bragg's law, the periodicity of the material is found to be ≈1.1 nm, corresponding to an interplanar distance of 0.55 nm.

Key interest for this confined form of germanane is the presence of luminescence in the visible range; this is in contrast to the bulk material which presents no luminescence due to the indirect nature of its bandgap. As such, methyl-terminated germanane is a very promising candidate for the fabrication of light-emitting diodes (LEDs). Indeed, current organic and nanocrystal-based LEDs suffer from low light extraction, which limits their conversion efficiency to 20%. This limitation is the result of isotropic emission of photons, which makes that most emitted light is lost due to total internal reflections. Here, due to its 2D geometry, germanane is expected to have anisotropic emission which may improve light extraction.[30] The photoluminescence (PL) peak of germanane appears around 700 nm (1.8 eV) around room temperature, see Fig. 2(a).

The full width at half maximum (FWHM) of the PL is ≈200 meV. Analysis of the temperature dependence of the PL reveals that, with decreasing temperature, the PL intensity increases [Figs. 2(e) and S1] and broadens [Figs. 2(f) and S2]. At high temperatures (>200 K), the ensemble PL signal is well fitted by a single Gaussian distribution [see Fig. S1(b)]; the energy of the transition appears at 1.8 eV, which corresponds to the predicted transition for the 2H phase of germanane.[19] PL measurements on a single flake at (250 K) reveals a PL signal with a similar linewidth, see Fig. 2(c). This suggests that the PL linewidth is the result of a homogeneous broadening. At low temperatures, a second contribution appears in the PL signal, see Fig. 2(b), and is responsible for the observed broadening of the PL

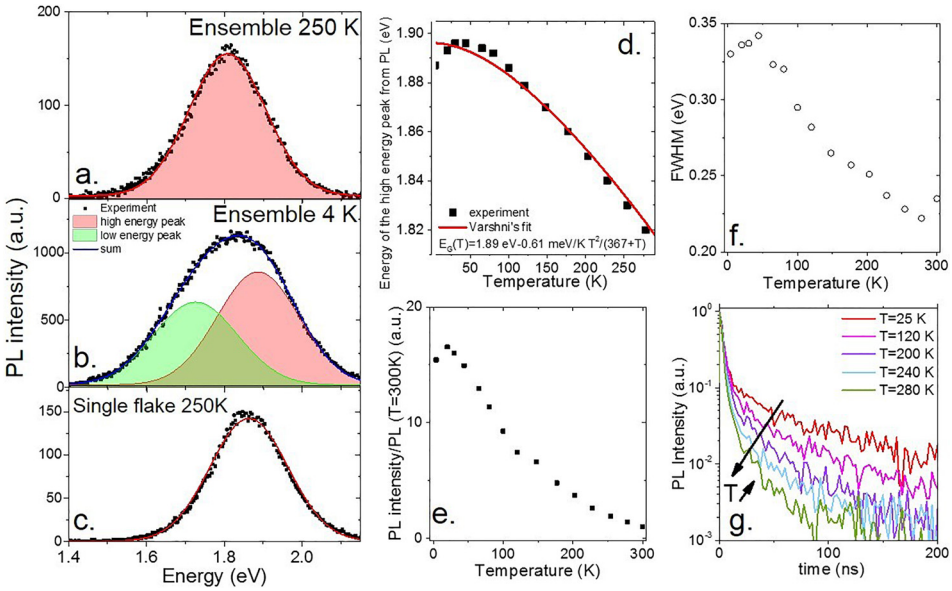

FIG. 2. Photoluminescence (PL) spectra of methyl-terminated germanane flakes: ensemble measurement at 250 K (a), ensemble measurement at 4 K (b), and (c) single flake measurement at 250 K [In all cases, experimental data are points and full curves are Gaussian (or two Gaussian sum) fit.] (d) Temperature dependence of the energy of the low energy peak and its Varshni's fit. (e) PL intensity as a function of temperature for a film of methyl-terminated germanane flakes. (f) Full width at half maxium (FWHM) of the PL signal as a function of temperature for a film of methyl-terminated germanane flakes. (g) Time resolved PL, integrated over the whole spectrum, for a film of methyl-terminated germanane flakes at various temperatures. The arrow shows the trend for the carrier decay as temperature is increased.

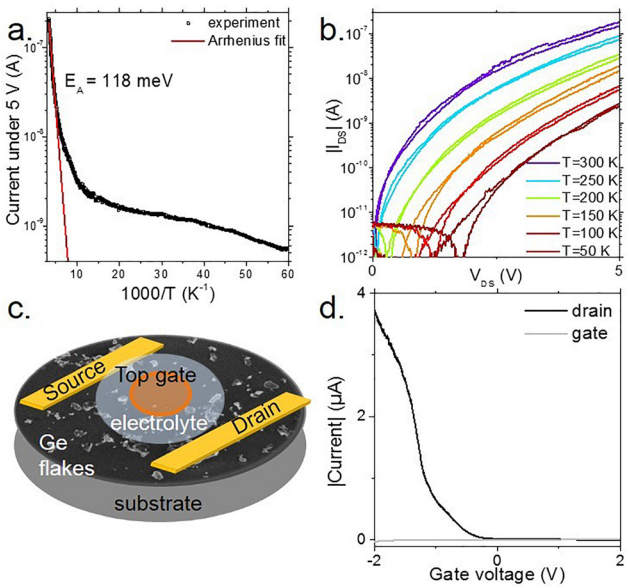

FIG. 3. (a) Diagram of an electrolyte gated field effect transistor, in which the channel is made of a dense film of methyl-terminated germanane flakes. (b) IV curve for a thin film of methyl-terminated germanane flakes at various temperatures. (c) Current as a function of temperature for a thin film of methyl-terminated germanane flakes at various temperatures under +5 V bias. (d) Transfer curve (drain and gate current as a function of the applied gate bias) for an electrolyte gated field effect transistor in which the channel is made of a dense film of methyl-terminated germanane flakes at room temperature. The drain source bias is set at −100 mV.

signal. Since the signal appears at an energy lower than the bandgap value, it is attributed to trap states. Note that depending on the relative weight of the two contributions, the PL peak may sometimes appears at lower energy in the literature.[15]

Fitting the high energy contribution (i.e., at the band edge) of the PL with a Varshni's expression, $E_G(T) = E_G(T = 0\,\mathrm{K}) - \frac{A \times T^2}{T+\theta}$, allows for the determination of the temperature dependence of the bandgap with A = 610 μeV/K and the phonon temperature $\theta = 367$ K. For the sake of comparison, the value of phonon temperature[31] has been found to be 374 K in the bulk, while the temperature dependence of the bandgap is slightly lower at 460 μeV/K.

Time-resolved PL [Figs. 2(g) and S3] reveals multiexponential behavior. At room temperature, three characteristic lifetimes can be extracted: 2 ns, 20 ns, and 100 ns. After 2 μs, the PL signal has fully decayed. We observe that the lifetime increases as temperature decreases. This is correlated with increased trap emission at low temperatures, suggesting that the rate of trap-assisted recombination is slower than band-to-band recombination. To further confirm this hypothesis, we have checked that the dynamics relative to the low energy part of the PL peak is slower than that relative to the high energy part of the PL peak, see Fig. S3(b).

To assess the electronic transport properties of germanane flake arrays, we constructed interdigitated electrodes using a conventional optical lithography method and drop-cast a dispersion of germanane flakes onto the electrodes. Figure 3(b) shows I-V characteristics of the germanane flake array at different temperatures. The arrays appear to be conductive, displaying decreasing conductance with decreasing temperature. Fitting the current-temperature curve to an Arrhenius law [Fig. 3(c)] allows for the extraction of an activation energy of 118 meV in the vicinity of room temperature. Because this activation energy is much smaller than one half of the bandgap—the expected value for intrinsic semiconductors—this suggests residual doping within the material. To determine the nature of this doping, we integrated the material in a field effect transistor. We use an ion gel electrolyte gating which has proven to be a viable approach for low gate bias field effect transistors made from colloidal nanocrystals[32] and 2D materials,[33] as shown in the schematic in Fig. 3(a). This strategy has been particularly successful for achieving gating in thick, heterogeneous films while allowing stable operation in ambient air.[34] The transfer curve [Fig. 3(d)] reveals p-type character (i.e., a rise of conductance under hole injection at negative gate biases) for the methyl-terminated germanane flake arrays; this is consistent with previous observations obtained using a back gated geometry.[26] The on/off ratio of the transistor reached a factor of 250 over only ±2 V of gate bias operation. It is also worth pointing that the turn-on voltage of the transistor is around 100 mV, which is very similar to the activation energy determined from the I-T curve. This suggests that the Fermi level of the material lies in the vicinity (100 ± 20 meV) of the valence band.

Under illumination, arrays of methyl-terminated germanane flakes display a positive photoresponse (i.e., a rise in conductance under illumination), as shown in Fig. 4(a). The time response of the device is typically below 100 μs with a weak temperature dependence. This corresponds in the frequency domain to a 3 dB cut-off frequency above 1 kHz, see Fig. 4(b). The power dependence of the photoresponse appears to present a power law dependency where the exponent is close to 0.5, as shown in Fig. 4(c). This suggests that the photocarrier lifetimes are limited by a bimolecular process[35,36] (i.e., band-to-band

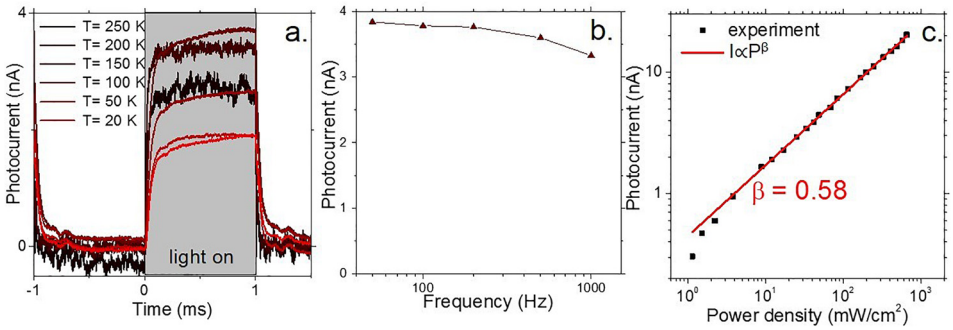

FIG. 4. (a) Current as a function of time, while the sample is illuminated by a pulse of light ($\lambda = 405$ nm; P ≈ 2 mW), at different temperatures. The measurement is made under a +5 V bias. (b) Frequency dependence of the photocurrent, at room temperature. (c) Current as a function of light incident power. Measurements are obtained at room temperature under 5 V bias.

recombination), rather than by trapping. This observation is consistent with the absence of traps in the PL spectrum at room temperature.

In conclusion, we have investigated the photoluminescence and electronic transport properties of methyl-terminated germanane flakes. The PL signal of the flakes was found to have two contributions: one from the band edge and the other that is attributed to trap states. The PL linewidth is found to have a homogeneous origin and a carrier lifetime in the range of 1–100 ns. Arrays of methyl-terminated flakes exhibit p-type conduction. The material is also photoconductive with a fast time response of the order of 100 μs, mostly limited by interband recombination.

See the supplementary material for information about material synthesis, material characterization, and additional transport measurements.

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The authors declare no competing financial interests.

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